Hybrid ionic liquid and polymer electrolytes for nanocrystalline dye-sensitized TiO_2 solar cells

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ABSTRACT

Alternative electrolytes for application in dye-sensitized TiO_2 solar cells were investigated. The electrolytes were prepared with NaI and I_2 as redox couple in a matrix consisting of poly(ethylene oxide-co-diethyleneglycolglicidyl methylether) and/or the ionic liquid N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide. Cyclic Voltammetry and Electrochemical Impedance Spectroscopy revealed that, increasing the relative amount of ionic liquid in the electrolytes, the impedance decreased and the ionic conductivity and the reversibility for the redox pair increased. For solar cells assembled with the polymer electrolytes, the efficiency for energy conversion decreased with light intensity, ranging from 3.2 to 1.4 % under 10 to 100 mW cm^{-2}. Using the ionic liquid electrolyte, the efficiency was ca. 1.8 %, independent of irradiation. For hybrid electrolytes, the best performance, considering mechanical stability and electrochemical properties, was achieved for an electrolyte consisting of 2:1 relative amount of polymer and ionic liquid. Solar cells assembled with this hybrid electrolyte presented, under 100 mW cm^{-2}, short-circuit current of 4.1 mA cm^{-2} and 1.4 % for overall efficiency (ca. 3.0 % under 10 mW cm^{-2}).

Keywords: dye-sensitized solar cells, ionic liquid, polymeric electrolytes, energy conversion.

1. INTRODUCTION

Dye-sensitized TiO_2 solar cells, DSSC, are a promising alternative for solar conversion devices from the 1990s.[1,2] DSSC consist of a dye-sensitized nanocrystalline TiO_2 electrode, an electrolyte containing a suitable redox couple (commonly, I^-/I_3^- dissolved in organic solvent) and a Pt coated counter-electrode (CE). The energy conversion results from a series of energy and charge transferences process in different interfaces, initiated by an electron injection from the excited state of the dye to the conduction band of the semiconductor. Reduction of the oxidized dye is achieved by iodine ions, and the resultant I_3^- ions must diffuse through the electrolyte to the CE. The redox couple is then regenerated, thus the cell operate in a regenerative mode for the light conversion process.[1-3] The performance and stability of these solar cells depend on several factors, and the electrolyte plays a very important role for cell operation.[4] Generally, DSSC are prepared using liquid electrolytes, which provide high mobility between the photo-electrode and CE redox couple and guarantees high efficiency for energy conversion, η of ca. 10 %.[1] However, a suitable sealing is necessary to avoid the leakage and/or volatilization of the solvent, which affects the performance of the device.

Several alternatives have been investigated to substitute the liquid electrolytes in DSSC, including polymers, ionic liquids, inorganic semiconductors or hole conductor organic materials.[5] However, in spite of the numerous studies already published, the reported values for light conversion efficiency are still lower than those obtained for liquid electrolytes. In general, electrolytes prepared with polymers based on ethylene oxide (PEO) with 10-15 % NaI and 2 % I_2 (wt), present ionic conductivity ranging from 10^{-6} to 10^{-5} S cm^{-1}. The efficiency of DSSC assembled with these polymeric electrolyte ranged from 1-1.5 % at 100 mW cm^{-2}, and 2-4 % under 10 mW cm^{-2}. Probably, the reduced mobility of I^-/I_3^- species in the polymeric medium affects the kinetic of dye regeneration (and this effect is even more important under high light intensity), reducing the efficiency of the solar cell.[2,3] Ionic liquids (IL) exhibit interesting properties for application in solar cells, such as high ionic conductivity, good chemical and and thermal stability, nonflammability and low volability.[6] IL can also be associated with polymers, resulting in hybrid electrolytes with good mechanical properties.[7]

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Recently, interesting studies have been published for DSSC assembled with electrolytes containing IL, as well as hybrid electrolytes consisted of IL and polymers. Using electrolytes prepared with 1-methyl-3-propylimidazolium iodide (MPII) or 1,2-dimethyl-3-propylimidazolium iodide (DMPII), DSSC exhibited current-densities ranging from 1.5 to 2.0 mA cm^{-2}.[8] DSSC assembled with a hybrid electrolyte consisted 1-methyl-3-[3-(trimethoxy-λ^4-silyl)propyl]-1H-imidazolium iodide and I_2, also including tetramethoxysilane, N-methylbenzylimidazolium (NMBI) and MPII, exhibited efficiency of 3.1 %.[9] Investigation of electrolytes containing the ionic polymer oligo(ethyleneoxide)-3-methylimidazolium chloride of different molecular weight revealed that the highest values of short-circuit current (I_{sc}), 6.8 mA cm^{-2}, and conversion efficiency of 3.1 % was achieved for DSSC assembled with the electrolyte containing higher molecular weight.[10] The influence of temperature on the performance of solar cells prepared with MPII electrolytes was investigated from 5-50°C and revealed higher efficiency, 2.6 %, at 41°C, which was related to redox species diffusion.[11] From the literature, the best result was an efficiency of 7.4 % (I_{sc} = 12.8 mA cm^{-2}) reported by Zakeeruddin et al.[12] for an electrolyte composed by 1-propyl-3-methylimidazolium iodide (PMII), 1-ethyl-3-methylimidazolium tricyanomethanide, NMBI and I_2. Good conversion efficiency, 7.72 %, was achieved for Fang and co-workers[13] for a 0.25 cm^2 DSSC assembled with NMBI, 1-hexyl-3-methylimidazolium iodide an 10 wt% of latent chemically cross-linked gel electrolyte precursor in 3-methoxypropionitrile. The device presented I_{sc} = 17.1 mA cm^{-2}, V_{oc} = 700 mV under AM 1.5 condition at 100 mW cm^{-2} irradiation.

Motivated by the development of alternative electrolytes for application in DSSC, we investigated electrolytes containing a new ionic liquid, N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide, $PYR_{13}TFSI$. This IL (Fig. 1) was already used as electrolyte in Li/V_2O_5 batteries, and exhibited electrochemical stability and good-performance.[14] In this contribuition, we studied its use in electrolytes for application in DSSC, combined with the redox couple I^-/I_3^- and the copolymer of 78 % poly(ethylene oxide) and 22 % diethyleneglycolglycidylmethylether, P(EO-DGME) (*Daiso Co. Ltd*., Osaka).

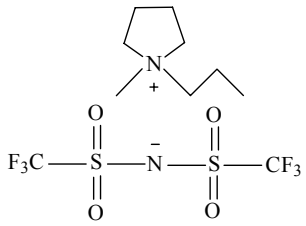

Fig. 1. Structure of the $PYR_{13}TFSI$ ionic liquid.[15]

2. EXPERIMENTAL DETAILS

2.1 Preparation and characterization of electrolytes

The electrolytes were prepared by dissolution in acetone of P(EO-DGME), $PYR_{13}TFSI$, NaI and I_2 (13 and 2.5 wt% in relation of IL and/or polymeric matrix weight, respectively). Hybrid electrolytes were also prepared, using different relative proportions of IL and copolymer. Films of the electrolytes were deposited onto substrates by casting, with evaporation under solvent saturated atmosphere.

Thermogravimetric analysis (TGA) was performed using a Thermogravimetric Analyzer model 2950 from TA Instruments. Measurements were done under inert atmosphere, using a continuous argon flow of 100 mL min^{-1} and heating rate of 10 °C min^{-1}. For TGA, films of the electrolytes were deposited on Teflon disks, then detached and dried under dynamic vacuum for 20 h to ensure elimination of solvent or water residues.

The ionic conductivity was estimated by Electrochemical Impedance Spectroscopy (EIS) measurements performed for films of the electrolytes deposited onto mirror-polished stainless steel blocking electrodes. Measurements were carried out in a MBraun dry box (28 ± 0.5 °C, [H_2O] < 0.0001 %, under argon atmosphere) using a Eco Chimie-Autolab PGSTAT 12 potentiostat with a frequency response analyzer (FRA) module. The frequency range was 10 to 10^6 Hz, with amplitudes of ± 10 mV over the open circuit potential (V_{OC}). The ionic conductivity values were calculated from Nyquist plots obtained by EIS, considering the thickness of the films.[16,17]

The electrochemical properties were investigated by Cyclic Voltammetry (CV) and EIS, using a symmetric thin-layer cell, where a film of the electrolyte was placed between two planar Pt coated glass-SnO_2:F (glass-FTO, Hartford glass, Rs $\leq$ 10 Ω cm^{-2}). The active area (1 cm^2) and the thickness (40 μm) of the films were controlled using adhesive tape. Measurements were performed using a two-electrode configuration (with reference circuited with counter-electrode). The EIS results were analyzed using Boukamp software. Preparing the cell, a film of the electrolyte was deposited on a Pt electrode by casting, at 60 °C. Then, the device was closed with another platinum CE, resulting in the configuration:

glass-FTO | Pt || electrolyte || Pt | FTO-glass

The Pt coated electrode (also used as CE in DSSC) was obtained by depositing a thin film of H_2PtCl_6 solution in isopropyl alcohol onto glass-FTO, followed by thermal treatment at 380 °C, for 10 minutes.

2.2 Application of electrolytes in solar cells

The photoelectrodes were prepared by deposition of TiO_2 film on glass-FTO electrode. A small aliquot of an aqueous suspension of nanocrystalline TiO_2 particles (diameter of ca. 25 nm, HPW Catalysts & Chemicals Ind. Co. Ltd.) and polyethylene glycol was spread onto the transparent electrode with a glass rod using adhesive tape as a spacer, followed by heating at 450 ^oC for 30 min. The samples were cooled to ~80 °C in a desiccator, and placed in 1.5 x 10^{-4} mol L^{-1} solution of the sensitizer dye *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), (Ruthenium-535, *Solaronix*) in absolute ethanol during 12 hours. After that, the electrodes were rinsed with ethanol and dried. A film of the polymer electrolyte was then deposited over the sensitized photoelectrodes by casting, at 60 °C. Then, the CE was pressed against the sensitized electrode coated with the polymer electrolyte. An adhesive tape (40 μm) was placed between the two electrodes, to control electrolyte film thickness and to avoid short circuit of the cell. The active area of the solar cells was 1.0 cm^2, and its final configuration was:

glass-FTO | TiO_2/dye || electrolyte || Pt | FTO-glass

The solar cells were characterized on an optical bench having an Oriel Xe lamp. Water and cut off filters were used to avoid IR and UV radiation, and the light intensity was varied using neutral density filters. The light intensity was measured with a Newport Optical Power Meter. Current density-potential curves were recorded under different light intensities with the potentiostat using the two-electrode configuration, with the photoelectrode connected as working electrode and the Pt electrode used as pseudo-reference (circuited with counter-electrode).

3. RESULTS AND DISCUSSION

3.1 Characterization of electrolytes

The thermal stabilities of the electrolytes were determined by TGA (Fig. 2).

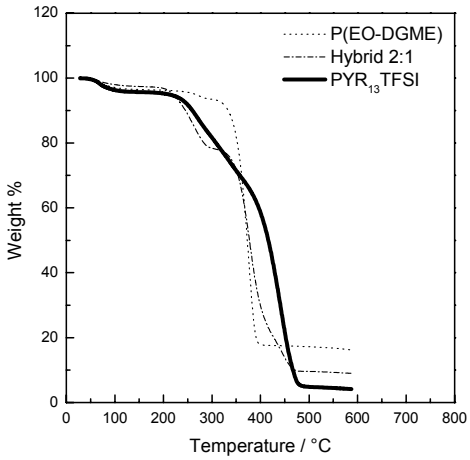

Fig. 2. TGA curves of electrolytes containing P(EO-DGME) and/or $PYR_{13}TFSI$, NaI and I_2.

The curve obtained for the polymeric electrolyte was similar to that determined to the pure copolymer P(EO-DGME) (data not shown), presenting only one mass loss step at 376 °C. On the other hand, higher values were found for the ionic liquid. The mass loss step was observed at 434 °C for the pure IL and at 443 °C for the samples containing the IL and the redox couple. The characteristics of both IL and copolymer could be observed for hybrid electrolytes. The electrolyte consisted of one part of IL for two parts of polymer, P(EO-DGME) : $PYR_{13}TFSI$ = 2:1, named hybrid 2:1, presented mass loss steps at 360 and 380 °C. Other relative compositions were also studied and presented gradual variation for both the mass loss steps, depending on the relative concentration of each constituent. Considering that most of the DSSC operate at temperatures below 120 °C, we conclude that a very satisfactory thermal stability was reached by these electrolytes for this technological application.

Figure 3 presents the variation of the ionic conductivities (σ) of the electrolytes containing 13 % NaI and 2.5 % I_2 as a function of IL content. The ionic conductivity was calculated from the bulk electrolyte resistance (R_b) value obtained from the Nyquist complex impedance diagram. Nyquist diagrams of EIS (data not shown) for the electrolyte containing P(EO-DGME) presented a semicircle at high frequency followed by straight line at low frequency. These characteristics can be related, respectively, to the electrolyte capacitance and diffusion of ionic species, as well as possible electrochemical reactions. This behavior is similar to those reported in the literature for PEO-based copolymer electrolytes.[17] For the ionic liquid electrolyte, the spectrum did not exhibit the semicircle and, in this case, R_b was estimated from the intercept at abscissa axis, the real impedance (named Z'). For these electrolytes, the R_b values decreased with increasing the IL content. In agreement, σ also increased with the ionic liquid content (Fig.3). The ionic conductivity for P(EO-DGME), $PYR_{13}TFSI$, and hybrid electrolytes were represented in Table 1. The reported data for pure $PYR_{13}TFSI$ (without the redox couple) presented the same magnitude, 2.8 mS cm^{-1}.[14] For hybrid electrolytes, the IL must act like a plasticizer, increasing polymer chain segmental motion, and, hence, the mobility of redox species, which increases σ values. It must be mentioned that, in fact, the ionic conductivity also depends on the salt concentration. For polymer electrolytes consisted of P(EO-DGME), the highest value was observed for 13-15 % NaI and 2 % I_2 (data not shown). In this study, the salt concentration was fixed at this condition.

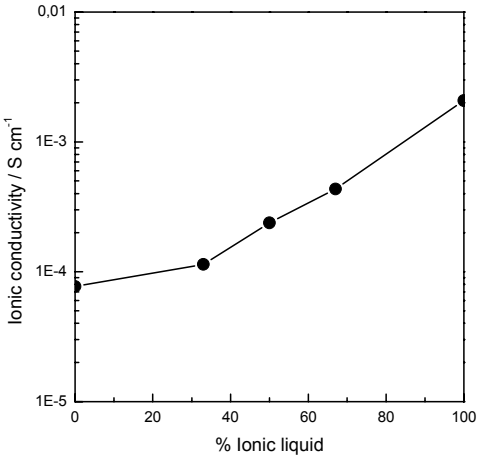

Fig. 3. Ionic conductivity of hybrid electrolytes consisting of NaI, I_2, P(EO-DGME) and $PYR_{13}TFSI$ for different relative amount of ionic liquid.

The electrochemical response of the electrolytes was investigated using thin-layer planar cells assembled with Pt electrodes. Figure 4 presents the cyclic voltammogram obtained for the polymer, IL and hybrid 2:1 electrolytes, as well as a blank consisted of the polymer sample without the redox couple. In general, the electrolytes presented an electrochemical stability window of 2.8 V and well-defined peaks for the redox couple. With the exception of the hybrid electrolyte which consisted of 2:1 P(EO-DGME):IL, for voltammograms determined at the same scan rate, the intensity current values increased with the IL amount in the electrolyte. This tendency was also observed for the cv obtained for other relative compositions (not presented in Fig. 4), Also, the difference between the anodic (E_p^A) and cathodic (E_p^C) peak potentials (ΔE_p) decreases with increasing the IL amount, indicating higher reversibility for the redox couple reactions in the electrolyte. These parameters are represented in Table 1 (potentials expressed in relation to the system Pt/I_3^-). These values are similar to those reported for I^-/I_3^- molten salts, where E_p^A = -0.1 V and E_p^C = 0.08 V.[18,19]

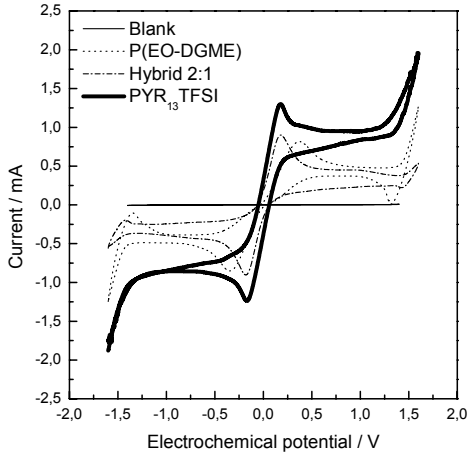

Fig. 4. Cyclic voltammograms of P(EO-DGME), hybrid 2:1 and $PYR_{13}TFSI$ electrolytes, measured with the scanning rate of 10 mV s^{-1}. The curve obtained for pure P(EO-DGME) (blank) was also shown.

Table 1. Characterization of electrolytes prepared with NaI, I_2 and different relative amount of polymer and ionic liquid: ionic conductivity (σ), anodic (E_p^A) and cathodic (E_p^C) peak potential values and peak separation (ΔE).

Electrolyte	**σ / mScm^{-1}**	**E_p^A / V**	**E_p^C / V**	**ΔE_p / V**
P(EO-DGME)	0.077	0.37	-0.35	0.72
Hybrid 2 : 1	0.11	0.16	-0.19	0.35
Hybrid 1 : 1	0.24	0.30	-0.30	0.60
Hybrid 1 : 2	0.43	0.24	-0.26	0.50
$PYR_{13}TFSI$	2.10	0.17	-0.18	0.35

Figure 5 presents the Nyquist diagrams from EIS measurements for the electrolytes. Comparison of the spectra revealed that the ionic liquid electrolyte presented smaller general impedance than the polymeric one. For hybrid electrolytes, the general impedance decreases with increasing the IL amount (data not shown in Fig. 5). Using Boukamp software, the experimental spectra obtained for electrolytes containing P(EO-DGME) could be fitted using the equivalent circuit $R_1(C(R_2O))$, represented as insert in Fig. 5. The symbols R and C describe resistance and capacitance, respectively; O, which depends on the parameters Y_0 and B, accounts for a finite-length Warburg diffusion (Z_{Dif}).[17] In Fig. 5, experimental data were represented by symbols and solid lines correspond to fit. The parameters obtained by fitting the impedance spectra for all the electrolytes investigated were represented in Table 2.

This equivalent circuit was already used to fit the spectra of other polymer electrolytes.[17] For P(EO-DGME) electrolytes, it also revealed excellent agreement with the experimental data, as observed for curves and the low values of χ^2 (Table2). The EIS spectrum of the $PYR_{13}TFSI$ electrolyte, which did not present capacitive behavior, could not be fitted with this equivalent circuit. Comparison of results represented in Table 2 revealed that the polymer electrolyte exhibited higher values for R_1 and R_2 parameters, which can be associated to the series resistance and to the resistance for charge transfer, respectively, as well as higher values for the capacitance (C) (except for hybrid 2:1). For hybrid electrolytes, R_1 and R_2 decreased with increasing the amount of ionic liquid (series resistance of 38 Ω). Also, this equivalent circuit cannot give a good representation of the experimental spectra for higher quantity of ionic liquid in the hybrid electrolytes, as can observed by the larger values of χ^2 (Table 2).

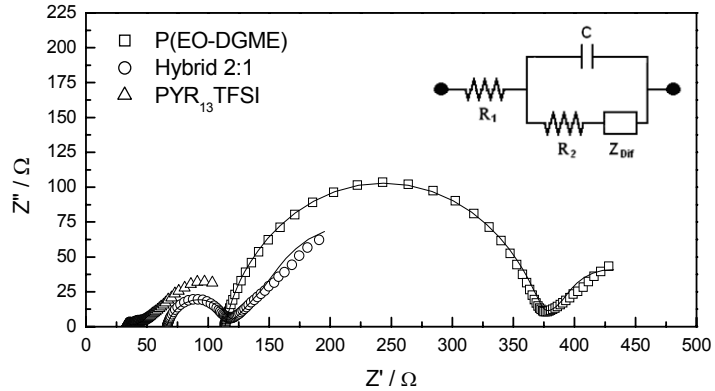

Fig. 5. Nyquist diagrams obtained by EIS for P(EO-DGME), hybrid 2:1 and $PYR_{13}TFSI$ electrolytes. Symbols represent the experimental data and solid line correspond to the fit obtained using the equivalent electric circuit (insert).

Table 2. Parameters obtained by fitting the impedance spectra of the P(EO-DGME) an hybrid electrolytes, using the equivalent circuit $R_1[C(R_2O)]$ (Figure 5).

Electrolyte	$\chi 2$	R_S / Ω	C / μF	R_1 / Ω	O	
					Y_0 / S	B / $s^{1/2}$
P(EO-DGME)	4.2×10^{-5}	114	40	259	0.075	7.3
Hybrid 2:1	2.6×10^{-4}	66	71	52	0.047	8.0
Hybrid 1:1	8.6×10^{-4}	28	11	18	0.024	8.6
Hybrid 1:2	4.7×10^{-4}	23	11	15	0.029	9.3

3.2 Characterization of solar cells

These electrolytes were investigated for application in dye-sensitized TiO_2 solar cells. The $PYR_{13}TFSI$, combined with NaI and I_2, presented excellent electrochemical response and high ionic conductivity. However, its mechanical properties results in the same disadvantage of usual liquid electrolytes. The electrolytes that included both P(EO-DGME) and $PYR_{13}TFSI$, hybrid 2:1, presented the best mechanical characteristics, comparable to those observed for the polymer electrolyte, but with higher ionic conductivity and better electrochemical response. Thus, this electrolyte was used for assembling DSSC. For comparison, solar cells were also prepared with polymer and ionic liquid electrolytes.

The current-potential curves (I-V) determined under 100 mW cm^{-2} irradiation for solar cells assembled using different electrolytes are represented at Fig. 6a. The solar cell assembled with ionic liquid electrolyte presented higher short-circuit current density (I_{sc}) and lower open circuit potential (V_{oc}) than cells prepared with the polymer electrolyte. Thus, besides the high photocurrent, the overall efficiency for energy conversion (η) was around 2 % (Table 3). Moreover, for intensity of radiation ranging from 10 to 100 mW cm^{-2}, the photocurrent increased almost linearly (Fig.6b) and the efficiency was practically constant $\eta = (1.8 \pm 0.2)$ %. For the cell assembled with the polymer electrolyte, the photocurrent increase was not linear with light intensity and the cell exhibited higher efficiency values under low irradiation. Using the hybrid 2:1 electrolyte, the solar cell exhibited similar values for I_{sc}, but intermediary values for V_{oc} parameters (Table 3). The high values for V_{oc} observed for DSSC assembled with polymer electrolytes, already discussed in literature[2,3], is related to Lewis acid-base interactions of PEO with TiO_2 surface. Probably, $PYR_{13}TFSI$ cannot present this kind of interaction, thus DSSC presented low values. Perhaps, for this reason, the overall efficiency exhibited by the cells prepared with the hybrid electrolyte was similar to those presented by the cell prepared with polymer electrolyte. Both of these cells presented better performance under low irradiation. This behavior, usually verified for DSSC assembled with polymer electrolytes, can be related to the reduced diffusion of redox species in the

electrolyte. Especially in high irradiation conditions, it can affect the kinetics of reaction for dye regeneration and, consequently, the overall efficiency of the device.[2,3] Probably, in spite of the better electrochemical properties exhibited by the hybrid electrolyte, the DSSC must be affected by the low open-circuit potential values.

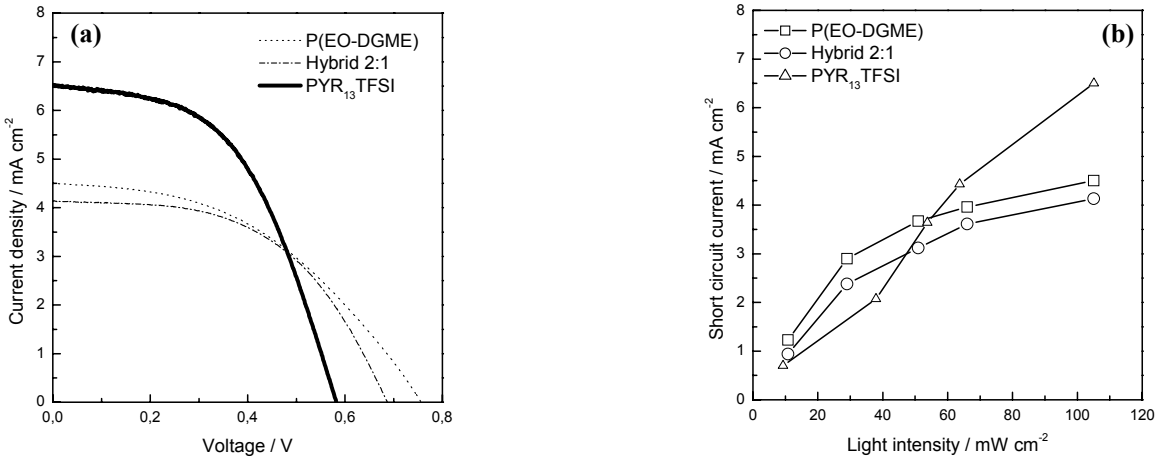

Fig. 6. TiO_2/dye solar cells (1.0 cm^2 of active area) assembled with electrolytes P(EO-DGME), hybrid 2:1 and $PYR_{13}TFSI$: I-V curves under 100 mW cm^{-2} (a) and variation of the short-circuit current with irradiation (b).

Table 3. Parameters determined from I-V curves for TiO_2 dye-sensitized solar cells assembled with the P(EO-DGME), hybrid electrolyte consisted of P(EO-DGME) and IL 2:1 and $PYR_{13}TFSI$ electrolytes.

Electrolyte	**Irradiation / mW cm^{-2}**	**I_{SC} / mA cm^{-2}**	**V_{OC} / V**	**η / %**
P(EO-DGME)	10	1.2	0.64	3.2
	100	4.2	0.76	1.4
Hybrid 2:1	10	0.9	0.56	2.8
	100	4.1	0.69	1.4
$PYR_{13}TFSI$	10	0.7	0.43	1.8
	100	6.2	0.58	1.9

4. CONCLUSIONS

Electrolytes containing the ionic liquid N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide were investigated for application in dye-sensitized TiO_2 solar cells. The $PYR_{13}TFSI$, combined with NaI and I_2, presented excellent electrochemical response and high ionic conductivity. However, its mechanical properties cause the same disadvantage of usual liquid electrolytes. Thus, this ionic liquid was combined with P(EO-DGME), resulting in hybrid electrolytes which utilizes the best qualities of both the materials. The hybrid electrolyte presented better mechanical characteristics, comparable to those observed for the polymer electrolyte, but with higher ionic conductivity and better electrochemical response. However, the DSSC prepared with this hybrid 2:1 electrolyte presented similar photocurrent but lower open circuit potential than those obtained using the polymer electrolyte and the same efficiency for energy conversion. Probably, in spite of the better electrochemical properties exhibited by the hybrid electrolyte, its performance in DSSC must be affected by the low open-circuit potencial values, perhaps due to a possible lower interaction with the TiO_2 surface.

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